Int'l Appl. No. Int'l filing date

PCT/FR2005/000342

February 14, 2005

## AMENDMENTS TO THE CLAIMS

- 1. (Currently amended) A catanionic membrane in the form of an organized solid bilayer comprising a lateral alternation of anionic surfactants with H<sup>+</sup> counterions and of cationic surfactants with cocrystallized OH counterions in which the mole fraction (MF): molar amount of anionic surfactants (Q<sub>AS</sub>)/(molar amount of anionic surfactants (Q<sub>AS</sub>) + molar amount of cationic surfactants (Q<sub>CS</sub>)) is greater than 0.5, said membrane forming a surface that is at least locally flat, characterized in that wherein said bilayer is stabilized with at least one polymer that is neutral and hydrophobic or of overall electrical charge opposite the effective charge of said catanionic membrane, said polymer being adsorbed onto said surface.
- 2. (Currently amended) The membrane as claimed in claim 1, characterized in that wherein the cationic and anionic surfactants are chosen from surfactants with a melting point of greater than 30°C.
- 3. (Currently amended) The membrane as claimed in claim 1-or 2, characterized in that wherein the cationic surfactants are chosen-selected from the monocatenary and bicatenary quaternary ammoniums of formulae (I) and (I'), respectively, below:

in which:

- $R_1$ ,  $R_2$  and  $R_3$ , which may be identical or different, represent a  $C_1$ - $C_4$  alkyl,  $C_1$ - $C_4$  hydroxyalkyl or  $(C_1$ - $C_4)$ alkyl ether radical,
- $R'_1$  and  $R'_2$ , which may be identical or different, represent a  $C_1$ - $C_4$  alkyl,  $C_1$ - $C_4$  hydroxyalkyl or  $(C_1$ - $C_4)$ alkyl ether radical,
- R'<sub>3</sub> and R'<sub>4</sub>, which may be identical or different, represent a saturated or unsaturated  $C_{8}$   $C_{24}$  hydrocarbon-based chain, a benzyl or  $(C_4$ - $C_{20}$ )alkylbenzyl radical or a  $(C_4$ - $C_{20}$ )alkyl ester group,
- $R_4$  represents a saturated or unsaturated  $C_8$ - $C_{24}$  hydrocarbon-based chain, a benzyl or  $(C_4$ - $C_{20}$ )alkylbenzyl radical or a  $(C_4$ - $C_{20}$ )alkyl ester group;

and mixtures thereof.

4. (Currently amended) The membrane as claimed in claim 3, characterized—in that wherein the  $C_1$ - $C_4$  alkyl radicals are methyl radicals.

- (Currently amended) The membrane as claimed in claim 3-or-4, characterized in that wherein the compounds of formula (I) are chosen from selected from the group consisting of dodecyltrimethylammonium hydroxide, cetyltrimethylammonium hydroxide, hydroxide, tetradecyltrimethylammonium stearyltrimethylammonium hydroxide, N-(2-carboxyethyl)-N,N-dimethyl-1-hexadecanaminium hydroxide, N-(2-hydroxyethyl)-N,Ndodecylcetyltriethylammonium hydroxide. dimethyl-1-hexadecanaminium hydroxide, triethylammonium hydroxide, stearyltriethylammonium hydroxide, tetradecyltriethylammonium dodecyltripropylammonium hydroxide, cetyltripropylammonium hydroxide, stearyltripropylammonium hydroxide and tetradecyltripropylammonium hydroxide.
- 6. (Currently amended) The membrane as claimed in claim 3-or-4, characterized in that wherein the compounds of formula (I') are chosen from selected from the group consisting of didodecyldimethylammonium hydroxide, didodecyldiethylammonium hydroxide, didodecyldibutylammonium hydroxide and dicetyldimethyltrimethylammonium hydroxide.
- 7. (Currently amended) The membrane as claimed in any one of the preceding elaimsclaim 1, eharacterized in that wherein the anionic surfactants are ehosen from selected from the group consisting of carboxylic acids with a C<sub>8</sub>-C<sub>24</sub> carbon-based hydrophobic chain with H<sup>+</sup> counterions and phosphates and sulfonates with H<sup>+</sup> counterions comprising one or two C<sub>12</sub>-C<sub>20</sub> alkyl chains.
- 8. (Currently amended) The membrane as claimed in claim 7, characterized in that wherein the anionic surfactants are chosen from selected from the group consisting of myristic acid, lauric acid and palmitic acid, phosphates, sulfates, benzyl sulfates and monocatenary glycerol monoesters.
- 9. (Currently amended) The membrane as claimed in any one of claims 3 to 8claim 3, characterized in that wherein the bilayers consist of:
- a) either of a cationic surfactant of formula (I) as defined in claim 3 and in which the radicals R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> are identical and represent a methyl radical and R<sub>4</sub> represents a hydrocarbon-based chain containing X carbon atoms, X being between 8 and 24 inclusive,

combined with a carboxylic acid <u>having a  $C_8$ - $C_{24}$  carbon-based hydrophobic chain with  $H^+$  counterions as defined in claim 6 in which the  $C_8$ - $C_{24}$  carbon-based hydrophobic chain contains  $X \pm 4$  carbon atoms;</u>

b) or of a cationic surfactant of formula (I') as defined in claim 3 in which the radicals R'<sub>1</sub> and R'<sub>2</sub> are identical and represent a methyl radical and R'<sub>3</sub> and R'<sub>4</sub> are identical and represent a hydrocarbon-based chain containing X carbon atoms, X being between 8 and 24 inclusive, combined with a carboxylic acid having a  $C_8$ - $C_{24}$  carbon-based hydrophobic chain with  $\frac{H^+}{C_{24}}$  counterions defined in claim 6 in which the  $C_8$ - $C_{24}$  carbon-based hydrophobic chain contains  $X \pm 4$  carbon atoms;

- c) or—a phosphate or a sulfonate comprising two identical alkyl chains containing X carbon atoms, X being between 8 and 24 inclusive, combined with a cationic surfactant of formula (I) as defined in claim 3 and in which the radicals R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> are identical and represent a methyl radical and R<sub>4</sub> represents a C<sub>8</sub>-C<sub>24</sub> alkyl chain; or
- d) or-a phosphate or a sulfonate comprising only one alkyl chain containing X carbon atoms, X being between 8 and 24 inclusive, combined with a cationic surfactant of formula (I') as defined in claim 3 and in which the radicals R'<sub>1</sub> and R'<sub>2</sub> are identical and represent a methyl radical and R'<sub>3</sub> and R'<sub>4</sub> are identical and represent a C<sub>8</sub>-C<sub>24</sub> alkyl chain.
- 10. (Currently amended) The membrane as claimed in claim 9, characterized in that wherein the bilayers are formed from a combination of cetyltrimethylammonium with OH counterions and myristic acid with H<sup>+</sup> counterions.
- 11. (Currently amended) The membrane as claimed in any one of the preceding elaimsclaim 1, eharacterized in that wherein the mole fraction  $Q_{AS}/(Q_{AS} + Q_{CS})$  is between 0.52 and 0.66.
- 12. (Currently amended) The membrane as claimed in any one of the preceding elaimsclaim 1, characterized in that wherein the bilayers also contain further comprise a minor molar amount of anionic surfactants with metal counterions.
- 13. (Currently amended) The membrane as claimed in any one of the preceding elaimsclaim 1, characterized in that wherein the neutral polymers are nonlipid polymers chosen from selected from the group consisting of polysaccharides, polyethylene glycols, polyoxyethylenes, polyvinylpyrrolidone, polyvinyl alcohols, oxyethylenated diblock polymers, block

copolymers based on ethylene oxide and propylene oxide, and triblock copolymers composed of hydrophilic-hydrophobic-hydrophilic blocks.

- 14. (Currently amended) The membrane as claimed in any one of claims 1 to 12 claim 1, characterized in that wherein the polymers with an overall electrical charge opposite the effective charge of the catanionic membranes are polymers of weakly negative electrical charge chosen from the group consisting of polyacrylates, polymethacrylates, polyethyl methacrylates, polybutyl methacrylates and polystyrenesulfonates, said polymers being substituted to more than 75% randomly with neutral water-soluble groups.
- 15. (Currently amended) The membrane as claimed in claim 14, <del>characterized in that</del><u>wherein</u> said polymer is a polyethylene glycol with a molecular mass of between 5000 and 50 000 Da.
- 16. (Currently amended) The membrane as claimed in any one of the preceding elaimsclaim 1, eharacterized in that wherein said polymers represent from 10% to 400% by weight relative to the total weight of the bilayer.
- 17. (Currently amended) The membrane as claimed in any one of the preceding elaimsclaim 1, characterized in that its wherein the mole fraction  $Q_{AS}/(Q_{AS} + Q_{CS})$  is between 0.55 and 0.58 and in that it is in the form of faceted hollow microcrystals.
- 18. (Currently amended) The membrane as claimed in claim 17, characterized in that itwherein the membrane is in the form of hollow polyhedra comprising from 12 to 30 approximately triangular faces.
- 19. (Currently amended) The membrane as claimed in claim 18, characterized in that itwherein the membrane is in the form of hollow icosahedra with an inner volume of between 0.1 and  $10 \,\mu^3$ .
- 20. (Currently amended) The membrane as claimed in claim 18-or-19, characterized in that wherein, within the organized solid bilayer of each of the faces of said microcrystals, the lateral alternation of the cocrystallized anionic and cationic surfactants is hexagonal, the flat part of said faces consisting solely of species containing H<sup>+</sup> or OH<sup>-</sup> counterions in stoichiometric amounts, whereas the apices of said faces are in the form of an internal semitorus predominantly formed from the anionic species in excess and in an amount sufficient to obtain an-a\_MF Q<sub>AS</sub>/(Q<sub>AS</sub> + Q<sub>CS</sub>) of between 0.55 and 0.58.

- 21. (Currently amended) The membrane as claimed in claim 20, characterized in that wherein the apex of each of the faces of a microcrystal forms a pore, together with the apices of the adjacent faces of the same microcrystal.
- 22. (Currently amended) The membrane as claimed in claim 17, characterized in that itwherein the membrane is in the form of fragments of hollow polyhedra constituting a stack of three-dimensional catanionic crystals in the form of a "pile of plates".
- 23. (Currently amended) A process method for preparing a catanionic membrane as defined in any one of claims 1 to 22claim 1, said process being characterized in that it comprises comprising the following steps:
- 1) a first step of formation of forming unilamellar vesicles by mixing, in an aqueous solvent of low conductivity:
- . a) a cationic surfactant (CS) with  $OH^{-}$  counterions in a molar amount  $Q_{CS}$  and
- b) one or more anionic surfactants (AS) in a molar amount  $Q_{AS}$  strictly greater than  $Q_{CS}$ , and corresponding to equations (1) to (3) below:

 $Q_{AS} = Q_{AS1} + Q_{AS2} \tag{1}$ 

 $Q_{AS1} = Q_{CS}$  (2) and

 $Q_{AS2} < 2(Q_{CS}) \tag{3}$ 

in which:

- $Q_{\text{AS1}}$  is the molar amount of an anionic surfactant with  $\boldsymbol{H}^{\text{+}}$  counterions
- $Q_{AS2}$  is the molar amount of an anionic surfactant with  $H^+$  counterions or with metal counterions, said surfactants having a carbon-based chain identical to that of the CS or of the AS with  $H^+$  counterions used in an amount  $Q_{AS1}$ ,

said mixture of cationic surfactant and of anionic surfactant being prepared at a temperature above the melting point of the chains of said surfactants;

2) a second step of obtaining flat aggregates formed from only one interdigitated or noninterdigitated crystalline molecular bilayer, by cooling the mixture obtained in the first step to a temperature below the melting point of the chains of the surfactants present in the mixture, thereby obtaining flat aggregates formed from only one interdigitated or noninterdigitated crystalline molecular bilayer; and

- 3) a third-step of stabilizing the crystalline molecular bilayers obtained above in the second step, by adding at least one neutral and hydrophobic polymer or a polymer of weakly negative overall electrical charge dissolved in an aqueous solvent of low conductivity, thereby stabilizing the crystalline molecular bilayers obtained above in the second step, said step being performed at a temperature below the melting point of the chains of the surfactants present in the mixture.
- 24. (Currently amended) The <u>processmethod</u> as claimed in claim 23, characterized in that, when the excess of anionic surfactant consists of anionic surfactants with metal counterions, then the first step of the <u>processmethod</u> comprises:
- a first substep in which the cationic surfactant with  $OH^-$  counterions is first mixed with the anionic surfactant with  $H^+$  counterions in an amount  $Q_{ASI}$  equal to  $Q_{CS}$ , and then
- a second substep in which the molar amount  $Q_{\text{AS2}}$  of anionic surfactant with metal counterions is then added.
- 25. (Currently amended) The <u>processmethod</u> as claimed in claim 23<del>- or 24</del>, eharacterized in that wherein the aqueous solvents have a conductivity of less than or equal to 1 MOhm.
- 26. (Currently amended) The <u>processmethod</u> as claimed in-any one of claims 23 to 25claim 23, characterized in that wherein the aqueous solvents are chosen from selected from the group consisting of water and glycerol, and mixtures thereof.
- 27. (Currently amended) The processmethod as claimed in any one of claims 23 to 26claim 23, characterized in that wherein, during the first step, the total concentration of surfactants in the solution is between 0.01% and 3% by weight relative to the total weight of said solution.
- 28. (Currently amended) The processmethod as claimed in any one of claims 23 to 27claim 23, characterized in that wherein, during the first step, the mixture is heated to a temperature of is greater than 30°C and less than 80°C.
- 29. (Currently amended) The processmethod as claimed in any one of claims 23 to 28claim 23, characterized in that, during the first step, further comprising adding at least one active substance is added to the mixture during the first step.

- 30. (Currently amended) The <u>processmethod</u> as claimed in claim 29, <u>characterized in that wherein</u> the active substance is <u>chosen from selected from the group consisting of pharmaceutical active principles, active substances for cosmetic purposes, cells and DNA or RNA fragments.</u>
- 31. (Currently amended) The processmethod as claimed in any one of claims 23 to 30claim 23, characterized in that wherein the volume fraction of polymer added to the mixture during the third step is between one and two times the total mass of the cationic and anionic surfactants.

## 32-33. (Cancelled)

- 34 (New) The method of claim 30, wherein the membrane is a faceted hollow polyhedron.
  - 35. (New) The method of claim 30, wherein the cells are bacterial cells.
- 36. (New) The method of claim 29, wherein the active substance is a chemical reactant, and further comprising diffusing reagents through pores of the catanionic membrane for chemical reactions with the chemical reactants.
- 37. (New) The method of claim 36, wherein the catanionic membrane is in the form of a faceted hollow polyhedron
- 38. (New) The method of claim 36, wherein the chemical reactions comprise precipitation and/or crystallization.
- 39. (New) The method of claim 34, wherein the active substance is a cosmetic, and further comprising:

flocculating the membrane in the form of bunches of polyhedra; and

absorbing the polyhedra onto surfaces of opposite surface electrical potential, thereby allowing efficient diffusion of the medicament.

- 40. (New) The method of claim 39, wherein the medicament is a cosmetic cream.
- 41. (New) A method of retaining volatile molecules by absorption and slow diffusion comprising mixing said volatile molecule with the catanionic membrane of claim 1, whereby the volatile molecule is retained.

- 42. (New) A method of vectorizing an active species comprising mixing the active species with the catanionic membrane of claim 1, whereby the active species is vectorized.
  - 43. (New) The method of claim 35, wherein said cells are encapsulated.
- 44. (New) The method of claim 30, wherein the active substance is DNA or RNA fragments and wherein said fragments are encapsulated.
- 45. (New) The method of claim 44, wherein the membrane is a faceted hollow polyhedron.